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Seiichi Takami, Yasuyuki Egashira, Itaru Honma, and Hiroshi Komiyama
Department of Chemical System Engineering, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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A hydrogen-terminated silicon surface was successfully converted to a surface covered with a monolayer of nitrogen. Nitridation was carried out in a vacuum chamber using either dimethylhydrazine $[H_2N–N(CH_3)_2]$ or ammonia at a pressure of 1 mTorr and at temperatures ranging from 400 to 600 °C. *In situ* x-ray photoelectron spectroscopy measurements revealed that the binding energy and the full width at half-maximum in the nitrogen spectra are the same as those in bulk Si_3N_4. Nitrogen content at the surface increased as the nitridation time increased and, below 500 °C, saturated at a value that approximately corresponds to a monolayer thickness. These results show the effectiveness of dry chemical processes for preparing uniform Si surfaces terminated with specific atoms or molecules other than hydrogen. © *1995 American Institute of Physics.*

Surface properties play a dominant role in the initial growth of films in thin-film processes. The increasing need for sophisticated film preparation processes, including epitaxial growth,[1,2] selective growth,[3,4] and trench filling,[5] requires that the surface be defined at an atomic level. Although an ultrahigh-vacuum system is a reliable means for controlling contamination, more economical processes are preferable for industrial applications. Current large scale integration processes prepare silicon wafers with hydrogen-terminated surfaces. A series of well-defined chemical processes, including the RCA cleaning method[6] and the HF treatment,[7] are widely used to create uniform (at the atomic level) and chemically stable hydrogen-terminated surfaces. To improve the quality of the deposited films, processing may include preparation of GaAs wafers with $(NH_4)_2S_x$,[8] exposing wafer surfaces to miscellaneous plasma atmospheres,[9] and spin coating the wafer surface with alcohol.[5] Ideally, preparation techniques should be optimized for each particular film deposition process. For this reason, chemical methods for coating surfaces with a monolayer of foreign atoms or molecules should be developed more extensively.

This letter describes an initial effort to chemically convert hydrogen-terminated silicon surfaces to nitrogen-terminated surfaces. Dimethylhydrazine (DMH) was used as a nitridation agent because we expected that its high chemical reactivity would allow us to achieve a low-temperature process. We also studied nitridation with ammonia (NH_3) because of its chemical simplicity.

We performed experiments on *p*-type ($\rho \sim 2.58\ \Omega\,m$) Si(111) wafers that were $0.5\times10\times10\ mm^3$ in size and that were pretreated by the following method: After removing the native oxide using buffered HF (1:7 $HF:NH_4F$), we immersed the samples for 10 min in a (1:1:5 $H_2O_2:NH_3:H_2O$) solution that was at 80 °C and then rinsed them with pure water. Next, we immersed the samples for 10 min in a (1:1:5 $H_2O_2:HCl:H_2O$) solution which was at 80 °C and then rinsed them again. Finally, we immersed the samples into 40% NH_4F for 5 min to remove the native oxide that had been formed during the pretreatment. This pretreatment terminates the silicon surface with a monolayer of hydrogen and ensures smoothness at an atomic level as well as chemical uniformity of the silicon surface.[10]

After pretreatment, the samples were immediately loaded on a sample holder in a transfer chamber, which was subsequently evacuated. The transfer chamber was attached to an x-ray photoelectron spectroscopy (XPS) chamber and to a nitridation chamber. This experimental apparatus allowed sequential *in situ* XPS measurements and nitridation steps. The XPS measurements were taken using Mg $K\alpha$ (1254 eV) radiation, and the binding energy spectra were calibrated using Au $4f_{7/2}$ (83.8 eV) and Cu $2p_{3/2}$ (932.8 eV) peaks.

After evacuating the transfer chamber, XPS measurements were used to analyze the pretreated surface of the sample. The sample was then transferred to the nitridation chamber and heated using an infrared lamp, reaching a predetermined temperature within 70 s. Nitridation was initiated by introducing a stream of DMH or NH_3 into the chamber. The time required to reach a predetermined pressure of DMH or NH_3 was no longer than 10 s. After the sample was exposed to DMH or NH_3 for a specified period, the gas stream was stopped and the pressure decreased to about 10^{-4} Pa in 10 s or less. The sample was nitrided in this manner several times. After each nitridation, the sample was moved to the XPS chamber to determine the surface composition, and then moved back to the nitridation chamber for the next nitridation step. A set of test wafers, which received the same experimental procedure except exposure to the nitridation gas, verified that, within the accuracy of our XPS measurements, the remaining experimental procedure as described above did not introduce any detectable change of the surface composition. Thus, the surface composition as a function of the accumulated time exposed to the nitridation gas, shows the temporal course of nitridation.

Figure 1 shows N 1*s* and Si 2*p* spectra of nitrided silicon exposed to DMH at 1 mTorr for various times. For the N 1*s* spectra, neither the binding energy nor the full width at half-maximum (FWHM) changed during the nitridation process. The binding energy and FWHM of the Si 2*p* spectra

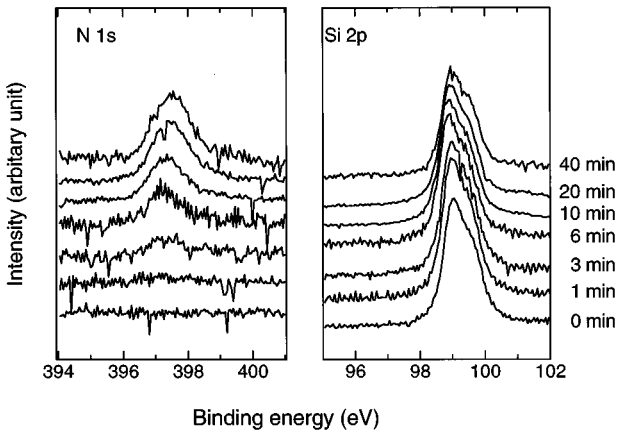

FIG. 1. XPS spectra of a silicon surface nitrided with 1 mTorr of dimethylhydrazine at 450 °C for various nitridation times.

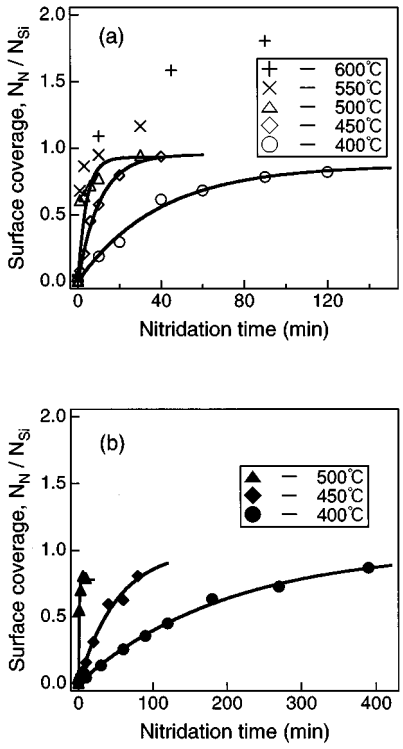

FIG. 2. Temperature and nitridation time dependence of nitride coverage from nitridation using (a) dimethylhydrazine and (b) ammonia.

also remained unchanged. Furthermore, neither temperature nor nitridation gas (i.e., NH_3 or DMH) affected the binding energy and FWHM. By taking the XPS measurements at a pressure of about 1×10^{-7} Pa, we excluded the possibility that these spectra were attributed to physisorbed molecules. Bischoff *et al.*[11] measured (using XPS) the binding energy of nitrogen atoms chemisorbed on Si surfaces, and showed that the binding energy of N 1*s* that is bound to three silicon atoms, $(Si)_3{\equiv}N$, is 397.4 eV, while that of surface amide, $Si{-}N{=}(H)_2$ is 398.6 eV. In addition, our measurements show that the FWHM for N 1*s* spectra are the same as those for bulk Si_3N_4 and confirm that the quantity of oxygen at the surface does not change beyond the background level of our XPS apparatus through the nitridation process. As a result, the N 1*s* spectra in Fig. 1 indicate that nitrogen atoms are bound uniformly with three silicon atoms during the course of nitridation. This leads to two conclusions: that this surface nitridation process preserves the chemical uniformity of the silicon surface created by our pretreatment technique, and that both DMH and NH_3 chemically modify hydrogen-terminated surface atoms to be bound with three nitrogen atoms per silicon atom, as XPS measurements revealed.

Figure 1 also shows the temporal evolution of the N 1*s* peak, that is the surface coverage of Si with chemically modified atoms as a function of nitridation time. In this study the surface coverage, N_N/N_{Si} was calculated from the intensity ratio of the XPS spectra assuming that Si_3N_4 with monolayer thickness covered a part of the silicon surface as concluded above. The attenuation length of photoelectrons for Si and Si_3N_4 used in these calculations were 27.3 Å (Ref. 12) and 26.8 Å (Ref. 13), respectively.

Figure 2 shows the temperature and time dependence of the surface coverage. The solid lines are fitted curves calculated assuming a first-order reaction and using the method of least-squares with two parameters, namely, saturated surface concentration and first-order reaction rates. These fitted curves agree well with our experimental data. Because the XPS measurements show that the quantity of oxygen does not exceed the background level, we can conclude that below 500 °C the surface coverage becomes a monolayer of Si_3N_4, independent of temperature, although the time required to achieve a monolayer increases as temperature decreases. On the contrary, at 550 and 600 °C the surface coverage exceeds a monolayer; furthermore, the data at 600 °C suggest that the surface coverage asymptotically approaches a double layer of Si_3N_4.

As confirmed using XPS, the chemical uniformity of the Si surface resulting from the pretreatment was preserved throughout the nitridation process. Therefore, the plateau region seen in Fig. 2(a) corresponds to a surface that is uniformly activated, and to a surface that, below 500 °C, does not grow beyond a monolayer. The surface coverage that corresponds to this plateau region is about 0.9, calculated from the XPS intensity ratio and assuming that the submonolayer Si_3N_4 uniformly covers the silicon surface. We also calculated this surface coverage using the ratio of nitrided silicon atoms to bulk silicon atoms $N_{Si\ nitride}/N_{Si\ bulk}$, and the calculated values again agree with experimental results. The calculated values for the surface coverage may include, however, errors from the attenuation length values used in this study. Nonetheless, from our results we conclude that for nitridation below 500 °C both DMH and NH_3 react with hydrogen-terminated Si surfaces to form Si_3N_4-like monolayers, and between 550 and 600 °C they continue to react beyond monolayer coverage.

In addition to the increase of surface coverage, Fig. 2 also indicates that the time constant of nitridation (i.e., nitridation rate) with DMH is five times shorter than that with NH_3. The difference is attributed to the reactivity of nitriding gases. Hydrogen-terminated Si surfaces are relatively stable, so that oxidation or nitridation proceeds very slowly even in air.[14] In the nitridation with NH_3, the rate-limiting step is the

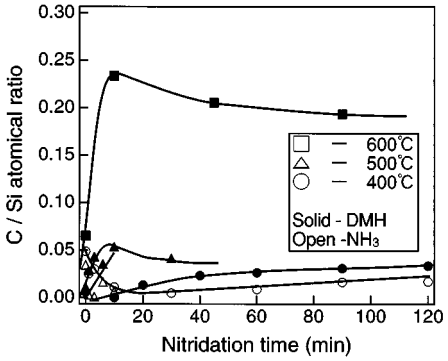

FIG. 3. Carbon contamination of nitrided silicon surfaces as a function of nitridation time and temperature using dimethylhydrazine or ammonia.

desorption of hydrogen from the silicon surface, since bare silicon surfaces have a large reactivity. On the other hand, because DMH is a derivative of hydrazine (H_2NNH_2), which is very reactive, DMH causes nitridation of hydrogen-terminated Si surfaces without the need for the desorption of hydrogen. The resulting nitridation rates with DMH are therefore higher than nitridation rates with NH_3. Because of this high reactivity, surface contamination during nitridation with DMH is reduced because bare Si surfaces, which are susceptible to contamination, are not required for nitridation.

Because DMH contains carbon atoms, there is a possibility of incorporating carbon into the silicon surface. We therefore measured the intensity ratio of the XPS spectra, N_C/N_{Si}, as a function of nitridation time and temperature with either DMH or NH_3 (see Fig. 3). Compared to nitridation with NH_3, nitridation with DMH causes the carbon content to increase if the temperature is above 500 °C. This carbon probably comes from methyl groups in the DMH. With the treatment temperature above 500 °C, this carbon will be captured in the silicon surface, forming silicon carbide. Below 450 °C, however, significant carbon increase was not detected. Therefore, in order to minimize carbon contamination, nitridation with DMH below 450 °C is preferable.

In conclusion, a dry chemical process for preparing well-defined Si surfaces is proposed. Hydrogen-terminated silicon surfaces were successfully nitrided below 500 °C using either DMH or NH_3, without destroying the surface uniformity (created by the pretreatment process), and forming nitride monolayers. Nitridation with DMH at lower temperatures (i.e., 400 °C) is possible because of its high reactivity with hydrogen-terminated Si surfaces. The present work suggests that this chemical modification method is applicable to many large scale integration processes because it does not require ultrahigh-vacuum or high temperatures (i.e., 900 °C and above), thus making it more economical than current techniques.

[1] M. Copel, M. C. Renter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[2] K. Sumitomo, T. Kobayashi, F. Shoji, K. Oura, and I Katayama, Phys. Rev. Lett. **66**, 1193 (1991).
[3] R. R. Rye, K.-M. Chi, M. Hampden-Smith, and T. T. Kodas, J. Electrochem. Soc. **139**, L60 (1992).
[4] K. Tsubouchi, K. Masu, and K. Sasaki, *Extended Abstracts of the 1992 International Conference on SSDM* (Japan Society of Applied Physics, Tsukuba, 1992), p. 208.
[5] N. Sato, T. Nakano, H. Yamamoto, and T. Ohta, Jpn. J. Appl. Phys. **32**, L110 (1993).
[6] W. Kern, J. Electrochem. Soc. **137**, 1887 (1990).
[7] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, Appl. Phys. Lett. **56**, 656 (1990).
[8] K. Ueno, T. Shimada, K. Saiki, and A. Koma, Appl. Phys. Lett. **56**, 327 (1990).
[9] K. Fujino, Y. Nishimoto, N. Tokumasu, and K. Maeno, J. Electrochem. Soc. **139**, 1690 (1992).
[10] G. S. Higashi, R. S. Becker, Y. J. Chabal, and A. J. Becker, Appl. Phys. Lett. **58**, 1656 (1991).
[11] J. L. Bischoff, F. Lutz, D. Bolmont, and L. Kubler, Surf. Sci. **251/252**, 170 (1991).
[12] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **17**, 911 (1991).
[13] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **17**, 927 (1991).
[14] D. Gräf, M. Grundner, R. Schulz, and L. Mühlhoff, J. Appl. Phys. **68**, 5155 (1990).